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SHEAR DEGRADATION OF POLYSTYRENE IN TOLUENE

by

ALI ASGHAR SARMASTI, 1939 -

A

THESIS

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Approved by

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ABSTRACT

The purpose of this study was to investigate the extent of flow degradation of narrow molecular weight distribution polystyrene samples under the conditions of laminar flow in capillary tubes. In all cases the solvent was toluene at 25°C, the polymer concentration was 0.1 weight percentage, and the calculated shear rate at the wall was in the range of 10^5 - 10^6 sec^{-1}. The extent of degradation was obtained by measuring the intrinsic viscosity [η] of the polystyrene samples before and after flow through capillary tubes having a wide range of length/diameter (L/D) ratios. The polystyrene samples here had molecular weight of 1.80×10^6, 8.6×10^5, 6.33×10^5, 4.11×10^5, 1.6×10^5 and 2×10^4, and molecular weight distributions were such that M_w/M_n did not exceed 1.10.

The experiments showed that the bulk of the polymer degradation occurred after the first pass of the solutions through the capillaries and that [η] approached an asymtotic value after several passes. The extent of degradation at shear rates of 10^5-10^6 sec^{-1} was independent of the L/D ratio for L/D of 800 to 1.75. Higher molecular weight samples showed a greater tendency to degrade than lower molecular weight samples down to molecular weights in the range of 1.5×10^5, below which no changes in [η] were observed. A correlation was not found below the extent of

degradation and the molecular weight distribution.

For the high molecular weight samples of polystyrene (750,000) k' was found to be 0.34 and increased to 0.44 for the 20,000 molecular weight sample.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to his advisor, Dr. K.G. Mayhan and Dr. G.K. Patterson for their guidance in the preparation of this thesis.

Thanks are extended to the Graduate Center for Materials Research for the use of its facilities and equipment.

The author would like to dedicate this dessertation to his brother, Mr. Ali Akhbar Sarmasti.

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I. INTRODUCTION

Although many articles and papers have been published on the degradation of long chain polymers in solution by hydrodynamic shear, there is little really definitive information concerning the relationship of shear rate, capillary length/diameter ratio, molecular weight distribution (M_w/M_n) and initial molecular weight. This study is directed toward an elucidation of these parameters.

II. LITERATURE REVIEW

The review of the literature will be confined to the degradation of linear polymers.

It is well established that long chain structures of polymer molecules undergo breakdown due to shear forces as the result of high speed stirring, milling, beating, grinding, turbulent flow or ultrasonic irradiation. Bestul and Belcher[1] carried out a number of experiments on the degradation from shear of a wide range of molecular weights of polyisobutylene in dichlorobenzene solutions (5, 10, and 15 weight per cent) for molecular weights ranging from 40,000 to 2,300,000. The solutions were forced through a capillary with a nominal shear rate of 65,000 sec^{-1} at 37.8°C. The results showed that very little degradation occurred for polymers having molecular weights below 500,000, but marked decreases were observed for polymers with higher molecular weights.

Harring and Zimm[2] also carried out a number of experiments on the degradation of polystyrene and of calf thymus DNA in both "good" and "poor" solvents. The solvents used in preliminary studies were redistilled reagent grade toluene, benzene, and methyl ethyl ketone. A comparison of equivalent data on the degradation of these solutions with those on later solutions using reagent solvents without additional purification detected no differences within

experimental error. Degradation was studied using (1) a high pressure capillary, (2) a speed device to force fluid at high pressure through the narrow annular region between a close fitting piston and cylinder, and (3) several laboratory homogenizers. Degradation was observed to follow roughly a first order rate law in all cases. For the first two devices mentioned, maximum shear rates were obtained which were used to estimate the critical shear stress for degradation by means of a semi-empirical relation. Estimated critical stresses were 3.5×10^{-6} dynes for polystyrene in "good" solvents, 4.0×10^{-7} dynes/cm^2 in "poor" solvents, and greater than 2.7×10^{-5} dynes/cm^2 for DNA is phosphate buffer solution. These values are roughly two orders of magnitude smaller than a simple theoretical estimate (based on bond strengths) for polystyrene and too small by a factor of 30 for DNA.

Morris and Schnurmann[3] reported an apparatus giving rates of shear of the order of 10^5 sec^{-1} under laminar flow conditions. Long-chain molecules of molecular weight above 100,000 (the nature of the polymer and solvents were not indicated by the author) were degraded.

Goodman[4] studied the degradation of polyisobutylene (Vistanex B-100) having an $\bar{M}_v$ of 1,740,000 in n-hexadecane (cetane) solutions (3-20 weight per cent). Degradation was produced by mechanical shearing action in a McKee cosistometer which is essentially a capillary viscometer in which

a single sample can be repeatedly passed through the capillary at rates of shear of 50,400, 33,000, 25,100 and 14,300 sec^{-1}. Goodman describes degradation as resulting from localization of mechanical energy by means of molecular entanglements present in concentrated solution. If sufficient energy is concentrated in this manner into a given bond, the bond breaks, resulting in a decrease in polymer molecular weight. His studies indicated that for a particular solution at constant temperature, the logarithm of the initial rate constant for the degradation is a linear function of the reciprocal rate of shear energy application per unit volume (J). At all concentrations studied in the range of 5-20 weight per cent, log K was the same function of 1/J, but such a plot for 3% solutions had a much greater negative slope. This indicates a decreased efficiency for the concentration of mechanical energy by the polymer molecules in less concentrated solutions.

Bestul[5] observed the shear degradation of polyisobutylene solutions in cetane. The polymers investigated were six unfractioned commercial Vistanex polyisobutene samples. The degradation was investigated as a function of concentration in the range of 5 to 20 weight per cent at nominal rates of shear from 9,000 to 66,000 sec^{-1}, in the temperature of 20 to 80°C. Initial viscosity average molecular weights varied from 490,000 to 2,520,000. A

decrease of shearing load with successive passes of the solution through the shearing capillary was taken as an indication of the occurrence of degradation. The extent of degradation decreased with increasing shear rate. The only shear load decrease shown for the lowest initial molecular weight polymer, 490,000, is a very slight one after the first passage through the capillary. Intrinsic viscosity measurements indicate that no degradation occurs in the solution of 490,000.

Bestul[6] also sheared solutions of 9.4 weight per cent Vistanex B-100 polyisobutene (1,740,000 $\bar{M}_v$) in cetane in the McKee consistometer at rates of shear of 66,000 and 33,000 sec^{-1}. In two companion runs, solutions of 9.4 weight per cent Vistanex B-100 polyisobutene ($\bar{M}_v$, viscosity average molecular weight = 1,740,000) in n-hexadecane were sheared initially at rates of 66,000 and 33,000 sec^{-1} and subsequently at interchanged rates. For these two runs the shear load decreased for 9.4 weight % Vistanex B-100 polyisobutene in cetane at 40° during the successive passes of the solution through the capillary. Shearing at 66,000 sec^{-1} before or after shearing at 33,000 sec^{-1} reduced $\bar{M}_v$ to 1,150,000. Shearing at 33,000 sec^{-1} before shearing at 66,000 sec^{-1} reduced $\bar{M}_v$ to 1,420,000. After shearing at 66,000 sec^{-1} subsequent shearing at 33,000 sec^{-1} effected no further $\bar{M}_v$ reduction. A critical molecular weight existed dependent on the severity of shearing, above which individual molecules in sufficient concentration

suffered degradation and below which shear degradation did not occur. This limit previously was found to be somewhat below 1,000,000 for unfractionated, undegraded polymer. Similar results were also obtained for low weight per cent solutions of polystyrene (an unfractionated sample about 5,000,000 $\bar{M}_v$) and 5 weight per cent solution of polymethacrylate (a top fraction of about 5,000,000 $\bar{M}_v$) both in α-methylnapthalene.[6] From these results, Bestul suggested that the degradation observed for the three different polymers occurred by the same common general mechanism described earlier. Literature reports of polyisobutene shear degradation[1, 5, 6, 7, 8] have been generally limited to bulk polymer and solution conditions of M_v greater than about 15,000 to 17,000. For higher polymer molecular weight and concentration, above the critical condition $(MV)_c$, a 3.4 power dependence of viscosity on molecular weight has been found[1,6-11] where M is $\bar{M}_v$ and V is the polymer volume fraction. In this region, substances show both pronounced non-Newtonian flow characteristics and flow shear degradation.[7] Nearly all the reported data are for concentrations above 3 per cent and most of it above 10 per cent. Little data are available at low concentrations where most polymer molecules are effectively separated.

The mechanism of degradation of poly (methyl methacrylate) has been proposed by several investigators. Kuhn's[12] interpretation was based on the random breaking theory that linear polymers degrade entirely by random scission of C-C bonds in the chains.

Simha[13] suggested that the mechanism of formation of monomers is due to the stepwise breaking away of the polymers at chain ends. Later, Blatz and Tobolsky[14] considered polymerization to be a stepwise process and they proposed that depolymerization was the reverse of polymerization. According to these workers, depolymerization would also be a stepwise process and in fact this is the same mechanism as Simha's except for a break at the ends of the chains.

Merrill, Mickley and Ram[15] studied the degradation of several high polymers (polyisobutylene, polystyrene, and polymethyl methacrylate) in solvents (cyclohexane, toluene, and ethylene dichloride) in two different types of experiments. In the first experiment, a variety of polymer solutions were splashed vigorously against the walls of a flask by a reciprocating motion. Concentrations ranged from 0.05 to 0.21 gm/dl at 30°C. In the second experiment, more viscous solutions of several polyisobutylene polymers in decalin at 30°C were passed through a coaxial cylinder viscometer in laminar flow at a shear rate in the annulus of 96,000 sec^{-1}. The concentrations ranged from

0.1 to 2.0 gm/dl and the viscosities from 4 to 27 centipoises. Based on the results of the splashing experiment, they reported that for polyisobutylene in toluene and cyclohexane, polystyrene in toluene and polymethyl methacrylate in ethylene dichloride, no significant degradation occurred if the degree of polymerization was 40,000 or less. This is equivalent to molecular weights of about 2.2×10^6 for polyisobutylene and about 4 million for the other two polymers. For polymers with higher degrees of polymerization, the fraction of residual molecular weight remaining after comparable periods of agitation decreased with increase in molecular weight. From the second experiment, they concluded that one pass of the more viscous decalin solutions through the viscometer was equivalent to 33 hours of splashing of toluene solutions of about the same concentrations.

Effect of degradation by pumping on normal stresses in polyisobutylene solution was studied by G.K. Patterson, H.C. Hershey, C.D. Green, and J.L. Zakin.[16] The effect of mechanical degradation and of solvent on the first normal stress differences were examined and compared with the effect on drag reduction in turbulent flow. Normal stresses were measured for dilute solutions of polyisobutylene in cyclohexane, toluene and n-heptane at high shear rates with a jet thrust apparatus in which the thrust tube was mounted on the frame of an analytical balance.

Molecular weight distribution curves and viscosity average molecular weights of the fresh and degraded solutions in toluene indicated that these effects were caused by the breakdown of small amounts of high molecular weight polymer, with only a small change in M_v.

Moore and Parks[17] studied mechanical degradation in a capillary viscometer with polystyrene (D.P.$>10^5$) for which the limiting viscosity number was 1400 ml/g . To eliminate the effects due to oxygen, a 0.070 per cent polystyrene solution in toluene was degassed and sealed under vacuum. The viscometer was rotated at intervals and a fixed volume was allowed to flow through the capillary. The rate of shear at the wall of the capillary of 0.80 mm diameter was 180 sec^{-1} at the start of the experiment. The flow time decreased from 550 sec to 462 sec after 28,220 passes through the capillary. A plot of flow time versus the logarithm of the number of passes gave a nearly straight line from 100 to 28,220 passes.

Sarswati, Roy-Chowdury, and Biswas[18] studied the degradation kinetics of butyl rubber in toluene and cyclohexane. Rubber solutions with $\sim 10^{-5}$ mole α,α-diphenyl-B-picrylhydrazyl (DPPH) were degraded by irradiation from an ultrasonic generator (with a 500-kc/sec quartz transducer) and then used both for viscosity determination and spectrophotometric estimation of DPPH. The degradation-rate curves obtained by these two independent methods were not

identical. With increasing viscosity of the solution, the rate of degradation decreased. Cavation of the media, a postulated mechanism for the degradation, was also reduced with increasing solution viscosity. Butyl rubber in two different solutions, initially having the same viscosity did not degrade at the same rates owing to the fact that since the viscosity changed at different rates during the degradation, the cavational intensity also varied. From the experimental data, it was concluded that all reported data for the limiting degree of polymerization are appreciably influenced by the viscosity of the solution, intensity of irradiation, and the initial molecule weight.

Gloeckner[19] pointed out that a mathematical method was developed for calculation of the decrease of the Staudinger index due to chain scission as a function of the broadness of the initial distribution and the exponent of the viscosity-molecular weight equation for polymers with a Schulz distribution. By comparing the theoretical curves with experimental curves from the literature, the value and the constancy of the cleavage rate can be determined. The initial velocity can also be obtained from the experimental ratio ($[\eta]_a/[\eta]_s$);($[\eta]_a$ and $[\eta]_s$ are the Staudinger indexes for the initial and degraded polymer, respectively), by using a correction factor that depends on the broadness of the initial distribution.

A. Kozo, N. Kuniaki, K. Tsuyoshi and N. Tsurutaro[20] studied dilute solutions (2 weight per cent) of high molecule weight polystyrenes (molecule weight 4×10^6 to 6×10^6) in butanone, benzene, and toluene. The polymer solutions were subjected to capillary flow, and the effect of the shear rate (1×10^4 to 5×10^5 sec^{-1}) on chain scission of the polymer was reported. In a given solvent, the degree of chain scission or the molecule weight depression increased with increasing shear rate. A poor, low viscosity solvent is more effective than a good, high viscosity in producing shear degradation. By using benzene-methanol mixtures as solvents having different solvent powers, but nearly equal viscosities, it was re-confirmed that poor solvents are more effective than good ones for the degradation of polymer in solution.

The degradation of polymethyl methacrylate in dilute solutions of a series of good and poor solvents (chloroform, benzene, tetrahydrofuran, heptane, acetone, butylacetate) during rapid stirring was studied.[21] Changes were followed by measurements of viscosity and light scattering. This indicated the tightness of the coiling of the polymer molecule in different solvents. The effect of the solvent on degradation was to be more pronounced in dilute solutions, in which the molecules do not interact with each other, but only with the solvent and within themselves. Degradation was faster when the polymer

molecules were extended, as in a good solvent.

A concentric cylinder viscometer has been used to measure the degradation of polyisobutane in cetane at high shear rates under laminar flow conditions.[22] Results were obtained for 10% solutions at 25, 40 and 80°C, and at several rates of shear up to 3×10^5 sec^{-1}. Temperatures and rates of shear were closely defined and measured. The degradation process was rapid and terminated at an equilibrium polymer molecular weight which was characteristic for a particular shear stress and decreased linearly with increasing shear stress.

III. EXPERIMENTAL

The purpose of this study was to investigate the effect of the initial molecular weight, number of passes through a capillary of various lengths, and calculated shear rate on the degradation of narrow distribution polystyrene samples in a good solvent (toluene) at 30°C. In all tests 0.1 weight per cent polymer solutions were used. This was done in order that all solutions would have the same number of repeat units per unit volume. By measuring the intrinsic viscosities of the polymers before and after testing, an estimation of the decrease in molecular weight was obtained.

A. Polymer Samples

Six narrow molecular weight polystyrene samples were used in this investigation. These samples were anionically prepared and their designations are presented in Table I.

B. Solvents

Spectrometric grade toluene (Fisher Scientific Co.) was used for all shear degradation and intrinsic viscosity measurements. The pertinent properties for toluene are presented in Appendix A.

C. Apparatus

The capillary-tube flow system is shown in Fig. 1.

TABLE I

POLYMER DESIGNATION

Polymer*	M_w	M_w/M_n	[η]
PS-1	180×10^4	<1.20	3.52
PS-2	86×10^4	<1.10	2.09
PS-3	63.3×10^4	<1.08	1.72
PS-4	41.1×10^4	<1.06	1.28
PS-5	16×10^4	<1.06	0.666
PS-6	2×10^4	<1.06	0.144

* These samples were furnished by Mellon Institute, Pittsburgh, Pa., and Pressure Chemical Co., Pittsburgh, Pa. Characterization by (a) light scattering, (b) membrane osmometry, and (c) viscometry.

Figure 1. Schematic Diagram of Degradation Test System.

1-6. Valves

7. Pyrex glass stopcock with adapter and teflon plug

8. Three-way Pyrex glass stopcock with teflon plug

9. 1/4-inch O.D. stainless steel tube

10. 1/8-inch O.D. stainless steel tube

11. 1/4-inch O.D. teflon tube

12. 1/4-inch O.D. glass tube with wintered glass filter at lower end

13. Reservoir: 1-inch O.D. stainless steel pipe

14. Aluminum jacket

15. Capillary tube

16. 1/4-inch O.D. brass tube

17. Graduate glass cylinder of 200 ml

18. Inlet water line from bath: 1/4-inch O.D. brass tube

19. Outlet water line to pump and bath: 1/4-inch O.D. brass tube

20. Brass connector: Swagelok fitting

21. Teflon cover with three straight bores

22. Brass tee

23. Inlet from nitrogen gas cylinder

24. Pressure-discharge line

25. High-pressure gauge (500 psi maximum)

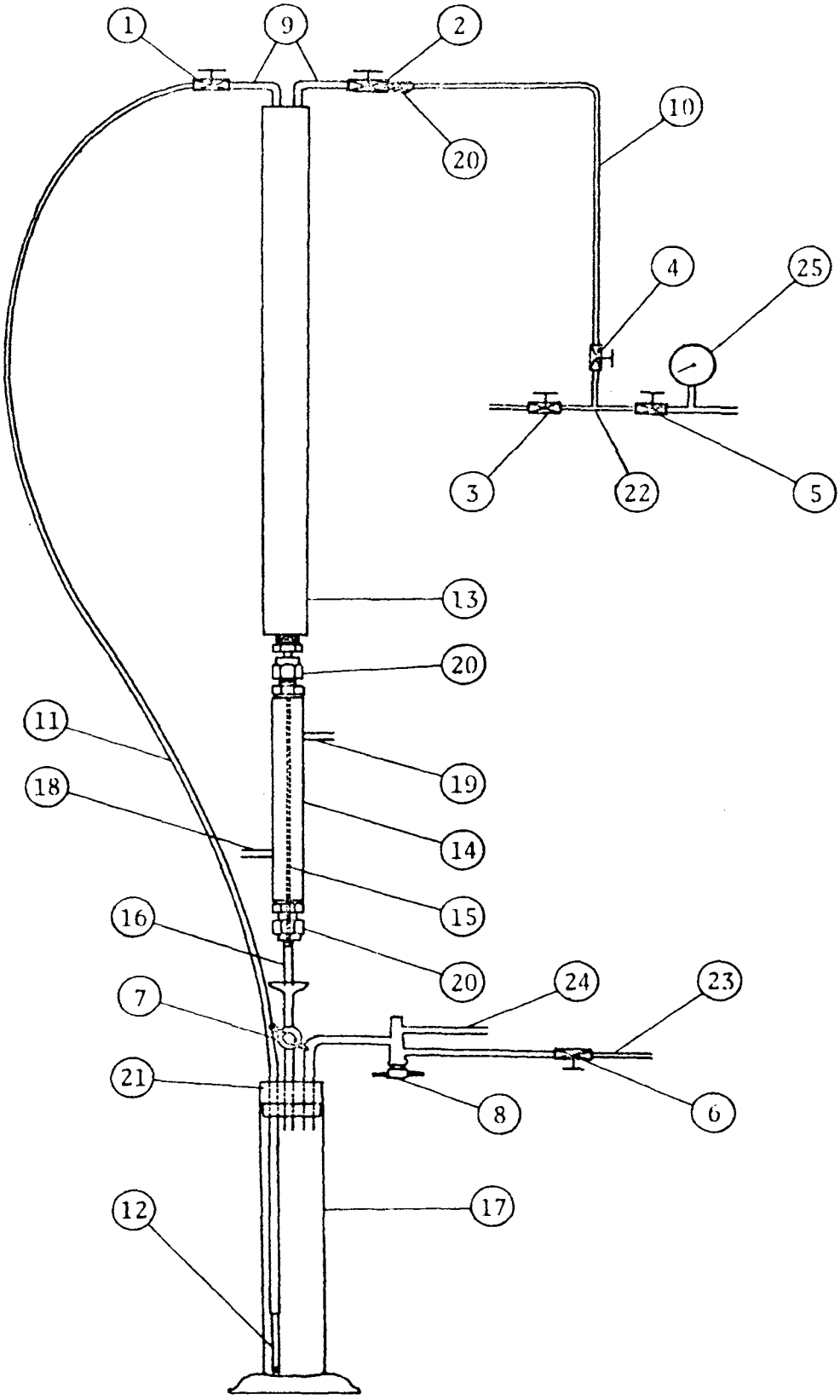

Figure 1. Schematic Diagram of Degradation Test System

In order to minimize contamination of the polymer-toluene solutions, the apparatus was constructed of No. 316 stainless steel and glass.

Two glass capillary tubes having diameter 0.0100 inches and 0.0067 inches and a 0.0080-inch brass orifice were used in this investigation. Different lengths of tubes were used in order to establish a range of length/diameter ratios. Table II gives the dimensions of the capillary tubes and of the orifice. Several attempts were made to fabricate orifices having diameters the same as the glass tubes. The smallest round orifice obtained was the one made from brass and having a diameter of 0.0080 inch. A scanning electron micrograph of this orifice is shown in Appendix B.

D. Procedure

1. Solution preparation. All solutions were made up to contain 0.1000 ± 0.0003 grams of polymer of any molecular weight per 100.0 ± 0.2 milliliters of toluene at 25°C in a 100 milliliter volumetric flask. The solutions were allowed to stand overnight in a dark cabinet after apparent dissolution. Angular disymmetry measurements showed the polymer to be dissolved.

2. Capillary Tube Flow Degradation. Referring to Fig. 1, the following procedure was used in all of the tests. The polymer solution was filtered and flowed into

TABLE II

CAPILLARY CHARACTERISTIC

Tube	Length in.	Diameter in.	Length/ Diameter
Glass Capillary No. 1			
	4.4375	0.0100	443.75
	1.0000	0.0101	100.00
	0.2500	0.0100	25.00
Glass Capillary No. 2			
	5.3750	0.0067	800.00
	0.6500	0.0067	100.00
	0.2500	0.0067	37.50
Brass Orifice			
	0.0140	0.0080	1.75

the reservoir from the graduated glass cylinder. The solution was then forced through the capillary tube by means of nitrogen pressure back into the glass cylinder. This procedure was repeated at a given pressure and 25°C until the solution was subjected to the desired number of passes. Different shear rates were obtained by varying the pressure for a given capillary.

The reservoir was constructed from 1-inch O.D. No. 316 stainless steel tubing. A chamber was constructed to allow a constant temperature fluid to be recirculated around the capillary.

3. Calibration of tubes. An accurate calibration of the capillary tubes is necessary in order to produce reliable measurements. Distilled toluene at 25°C was used as the calibration fluid in this work. Since the fluid was discharged from the capillary tube at atmospheric pressure it was possible to measure the pressure drop using an accurate pressure gauge on the inlet side of the system. The diameter of the tube was calculated by means of the Hagen-Poiseville equation for a number of pressures for each length of tube and the average value was taken as the diameter. These data and a sample calculation are presented in Appendix D along with a typical calibration curve. All of the tests reported here were performed at a Reynold's Number of 1800 and the applied nitrogen pressure was determined from the calibration curves at this point.

The data obtained are tabulated in Table III (also see Appendix D for a sample calculation).

The value of diameters thus calculated from equations (1), (2), and (3) were listed as the diameter for the capillary tubes for the particular data point.

$$D = 2(8QL\mu/\pi\Delta P)^{1/4} \tag{1}$$

$$\frac{1}{\sqrt{f}} = 4.0 \log(N_{Re}\sqrt{f}) - 0.40 \tag{2}$$

$$D = (8Q^2\rho/\pi^2 g_c \Delta P)^{1/4} \text{ (orifice)} \tag{3}$$

where,

D = diameter, ft.

Q = flow rate

L = capillary length, ft.

μ = absolute viscosity, lbm/ft.sec.

ΔP = pressure drop across the tube, lb_f/ft^2

f = friction factor, dimensionless

N_{Re} = Reynold's number, dimensionless

g_c = 32.2 $lbm/lb_f \cdot$ $ft/(sec)^2$

π = geometric constant (=3.1416)

Using the newly calculated diameter, the average shear rate at the tube wall may be calculated from the relation:

$$\left(\frac{-dv}{dr}\right)_w = \frac{4Q}{\pi R^3} = \frac{8V}{D} \tag{4}$$

TABLE III

CALIBRATION OF THE TUBE DATA

A. Nominal 0.0070 - in glass capillary tube
tube length = 5.375 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
20	0.0327	0.0067	430
40	0.0665	0.0067	875
50	0.0769	0.0066	1050
75	0.1137	0.0067	1490
100	0.1472	0.0068	1820
150	0.1710	0.0067	2320
200	0.1882	0.0067	2550
300	0.2310	0.0067	3140
400	0.2700	0.0067	3680

Average diameter = 0.0067 in.

tube length = 0.67 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
10	0.0860	0.0067	1170
15	0.0115	0.0067	1570
20	0.1400	0.0067	1900

Average diameter = 0.0067 in.

TABLE III
(CONTINUED)

tube length = 0.25 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
5	--	0.0067	940
10	0.1024	0.0067	1490
15	0.1550	0.0067	2000
20	0.1783	0.0067	2420

Average diameter = 0.0067 in.

B. Nominal 0.0100 - in glass capillary tube
tube length = 4.4375 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
10	0.0834	0.0101	750
20	0.1600	0.0100	1400
30	0.2100	0.0101	1850
40	0.2388	0.0100	2110
50	0.2500	0.0104	2270
100	0.3300	0.0102	3075
150	0.4100	0.0100	3725
200	0.4900	0.0100	4450
300	0.6000	0.0100	5450
400	0.7100	0.0100	6450

Average diameter = 0.0100 in.

TABLE III
(CONTINUED)

tube length = 1.00 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
10	0.230	0.0102	2100
15	0.278	0.0101	2530
20	0.312	0.0101	2840

Average diameter = 0.0101 in.

tube length = 0.25 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
5	0.	0.0100	1800
10	0.315	0.0100	2830
15	0.388	0.0100	3515
20	0.440	0.0101	4000

Average diameter = 0.0100 in.

C. Nominal 0.0080 - in Brass orifice

tube length = 0.0140 in.

Pressure Gauge Reading (Psi)	Flow Rate (g/sec)	Calculated Diameter (in.)	Reynold's Number
2	0.1528	0.0079	1740
3	0.1915	0.0080	2180
5	0.2488	0.0080	2830

Average diameter = 0.0080 in.

where,

Q = flow rate, cube ft/sec

R = radius of tube, ft

D = diameter, ft

V = velocity of flow along the tube ft/sec

The calculated data are shown in Appendix F and used as a parameter in the degradation test under different shearing conditions.

4. Recovery of polymer. After the completion of the flow tests the polymer solution was transferred to a freeze drying flask, cooled to liquid nitrogen temperatures and allowed to freeze dry to a constant weight. In several instances the solvent was partially evaporated using a low temperature vacuum evaporator prior to the final drying. The dried polymer was stored in clean dry glass bottles pending intrinsic viscosity determination.

E. Intrinsic Viscosity Determination

Intrinsic viscosity [η] determinations were made utilizing a Cannon-Ubbelohde dilution viscometer. A Number 50 viscometer with a 20 milliliter dilution bulk was used for all of the tests. The efflux time for toluene at 30.00 ± 0.01°C was 160.9 ± 0.1 seconds. Kinetic energy effects were considered negligible and were not taken into account in the calculations. Standard viscosity

dilution determination procedures were followed in making the determinations. The initial concentrations were such that before dilution the relative viscosities were approximately 2.0. A typical intrinsic viscosity plot is presented in Appendix F. $[\eta]$ and the molecular weight were related by $[\eta] = KM_v^a$, where K and a are the Mark-Houwink coefficients. At 30°C, for the polystyrene-toluene system, K = 0.978 and a = 0.73.

IV. RESULTS AND DISCUSSION

Polystyrene solutions, 0.1 weight per cent, in toluene were tested in glass capillary tubes at room temperature at various calculated average wall shear rates. Intrinsic viscosities were used to derive viscosity average molecular weights for the six samples of polystyrene which were tested. Table IV shows the polymer sample specification and the molecular weights calculated from the equation

$$[\eta] = KM_V^a \qquad (5)$$

(5) for polystyrene in toluene at 30°C. The constants calculated for this system from the Huggins equation are also listed.

Harrington and Zimm's capillary shearing experiments[2] of dilute polystyrene solution ($\bar{M}_V = 1.07 \times 10^7$ and 3.72×10^6) in toluene, conducted over the temperature range from 15 to 45°C, disclosed no evidence for temperature dependence of the degradation process. Furthermore, the temperature at which thermal degradation of polystyrene becomes appreciable is found[25] to be 276°C. Therefore, the thermal contribution to degradation should be negligible at room temperature according to Harrington and Zimm. This observation appears to be correct for this work and

the degree of chemical degradation at room temperature was not detectable.

The Reynold's number in this study was maintained at 1800, which is generally accepted as being in the laminar flow region. On the basis of these parameters, any polymer degradation must be a result of shear stresses at the wall of the capillary or other mechanical degradation. Significant differences in degradation were observed for any of the measurements with respect to L/D ratio, but a small residual effect seems to exist after one pass. It appears that in all cases the extent of degradation at shear rates of $\sim 10^5 - 10^6$ sec^{-1} is independent of the L/D ratio within the limits of these experiments.

These measurements suggest that it is the shear stresses at the entrance of the capillary that result in polymer degradation and not the average shear stresses at the wall. Correlations based upon the average calculated shear stresses at the wall serve as a convenient index, but do not provide a fundamental relationship between degradation and shear stress. The shear stresses at the entrance are not easily computable since small changes in the entrance geometry are difficult to characterize.

Tables IV through IX list experimentally obtained values of k', the Huggins constant. For high molecular weight polystyrene in toluene, k' is equal to about 0.34 which is equal to many values previously reported.

TABLE IV

VISCOSITY AVERAGE MOLECULAR

WEIGHTS OF POLYSTYRENE

Polystyrene Specification	[η] dl/g	k'	k"	k' + k"	M_v
PS-1	3.515	0.340	0.160	0.500	1.9×10^6
PS-2	2.090	0.328	0.167	0.495	9.36×10^5
PS-3	1.710	0.325	0.171	0.496	6.86×10^5
PS-4	1.280	0.321	0.185	0.506	4.68×10^5
PS-5	0.666	0.310	0.187	0.497	1.87×10^5
PS-6	0.144	0.4404	0.0671	0.508	2.00×10^4

TABLE V

SHEAR DEGRADATION IN 0.0100 IN. ID LONG (L = 4.4375 IN.)

GLASS CAPILLARY TUBE AT 28 PSI (CALCULATED SHEAR RATE =

1.40×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o - [\eta]$ dl/g	k'	k"	k' + k"	$M_v \times 10^{-4}$
PS-1	1	3.180	0.325	0.338	0.159	0.497	170.00
($[\eta]_o$ = 3.515)	20	3.050	0.465	0.335	0.165	0.500	160.00
PS-2	1	1.960	0.13	0.330	0.171	0.5010	86.00
($[\eta]_o$ = 2.090)	20	1.910	0.18	0.338	0.162	0.5040	82.80
PS-3	1	1.630	0.08	0.350	0.150	0.500	66.30
($[\eta]_o$ = 1.71)	20	1.570	0.14	0.359	0.146	0.505	62.80
PS-4	1	1.175	0.105	0.370	0.127	0.497	41.70
($[\eta]_o$ = 1.28)	20	1.140	0.140	0.365	0.135	0.500	40.20
PS-5	1	0.588	0.078	0.310	0.188	0.498	15.80
($[\eta]_o$ = 0.666)	20	0.586	0.080	0.315	0.180	0.495	15.70
PS-6	1	0.1440	0	0.4400	0.067	0.507	2.00
($[\eta]_o$ = 0.144	20	0.1435	0	0.4401	0.057	0.497	2.00

TABLE VI

SHEAR DEGRADATION IN 0.0067 IN. ID LONG (L = 5.375 IN.)

GLASS CAPILLARY TUBE AT 100 PSI (CALCULATED SHEAR RATE =

3.13×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o-[\eta]$ dl/g	k'	k"	k' + k"	$M_v \times 10^{-4}$
PS-1	1	3.105	0.415	0.330	0.165	0.495	165.00
($[\eta]_o$ = 3.515)	20	2.830	0.585	0.320	0.180	0.500	144.00
PS-2	1	1.930	0.16	0.328	0.180	0.508	84.00
($[\eta]_o$ = 2.09)	20	1.860	0.23	0.332	0.173	0.505	77.30
PS-3	1	1.610	0.10	0.356	0.142	0.498	65.10
($[\eta]_o$ = 1.71)	20	1.540	0.17	0.356	0.148	0.504	61.20
PS-4	1	1.160	0.23	0.370	0.133	0.503	41.00
($[\eta]_o$ = 1.28)	20	1.110	0.17	0.370	0.135	0.505	38.60
PS-5	1	0.581	0.085	0.380	0.117	0.497	15.50
($[\eta]_o$ = 0.666)	20	0.580	0.084	0.375	0.122	0.497	15.50
PS-6	1	0.144	0.00	0.4405	0.0575	0.508	2.00
($[\eta]_o$ = 0.144)	20	0.144	0.00	0.4400	0.058	0.498	2.00

TABLE VII

SHEAR DEGRADATION IN 0.0101 IN. ID SHORT (L = 1.0 IN.) GLASS CAPILLARY TUBE AT 8 PSI (CALCULATED SHEAR RATE = 1.40×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

A.

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o-[\eta]$ dl/g	k'	k"	k' + k"
PS-2	1	1.97	.12	0.324	0.172	0.496
($[\eta]_o$ = 2.09)	20	1.90	.19	0.327	0.170	0.497

SHEAR DEGRADATION IN 0.0101 IN. ID GLASS CAPILLARY TUBE (L = 0.25 IN.) AT 5 PSI (CALCULATED SHEAR RATE = 1.40×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER 1800)

B.

Sample	No. Passes	η dl/g	$[\eta]_o-[\eta]$ d/g	k'	k"	k' + k"
PS-2	1	1.96	.13	0.328	0.169	0.497
($[\eta]_o$ = 2.09)	20	1.91	.18	0.335	0.163	0.498

TABLE VIII

SHEAR DEGRADATION IN 0.0067 IN. ID GLASS CAPILLARY TUBE (L = 0.67 IN.) AT 18 PSI (CALCULATED SHEAR RATE = 3.13×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

A.

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o-[\eta]$ dl/g	k'	k"	k' + k"
PS-2	1	1.94	0.15	0.330	0.169	0.499
($[\eta]_o$ = 2.09)	20	1.86	0.23	0.339	0.166	0.505

SHEAR DEGRADATION IN 0.0067 IN. ID GLASS CAPILLARY TUBE (L = 0.25 IN.) AT 13 PSI (CALCULATED SHEAR RATE = 3.13×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

B.

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o-[\eta]$ dl/g	k'	k"	k' + k"
PS-2	1	1.96	0.13	0.328	0.169	0.497
($[\eta]_o$ = 2.09)	20	1.91	0.18	0.335	0.163	0.498

TABLE IX

SHEAR DEGRADATION IN 0.0080 IN. ID BRASS ORIFICE (L - 0.0140 IN.) AT 2.20 PSI (CALCULATED SHEAR RATE = 2.22×10^5 SEC.$^{-1}$, REYNOLD'S NUMBER = 1800)

Sample	No. Passes	$[\eta]$ dl/g	$[\eta]_o - [\eta]$ dl/g	k'	k"	k' + k"
PS-2	1	1.98	0.11	0.330	0.167	0.497
($[\eta]_o$ = 2.09)	20	1.92	0.11	0.330	0.165	0.495

However, the low molecular weight polystyrene (sample PS-6, $\bar{M}_v$ = 20,000) gave k' = 0.44. A similar increase in k' for polystyrene at molecular weights below 50,000 has been reported by Simha and Zakin[27] and by McCormick.[28] A plot of k' versus M_v for different investigations is shown in Figure 4.

Figures 2 and 3 show that [η] reaches an asymptotic value after the first several passes and that no further changes are noted for any of the polymer samples, even after 20 passes. The M_v of PS-1 changes from 1.9 x 10^6 [η_o = 3.515] to 1.44 x 10^6 [η = 2.830] after 20 passes in a 0.0067 in. diameter capillary. Samples PS-2, PS-3, PS-4, and PS-5, all of which have lower molecular weight than PS-1, show smaller initial decreases in [η] before reaching a constant value. These findings indicate that for a given M_v, the tendency to degrade is a function of the molecular weight distribution as well as the average molecular weight since this distribution may be specific for a given method of polymerization of fractionation; the tendency to degrade would be a function of the polymerization method.

For the shearing test in the 0.0100 in. (L = 4.4375 in.) and 0.0067 in. ID (L = 5.375 in.) glass tubes at 1.40 x 10^5 sec^{-1} and 3.13 x 10^5 sec^{-1}, respectively, the data shown in Tables V and VI reveal that for equal pass numbers, the lower the initial molecular weight, the less the extent

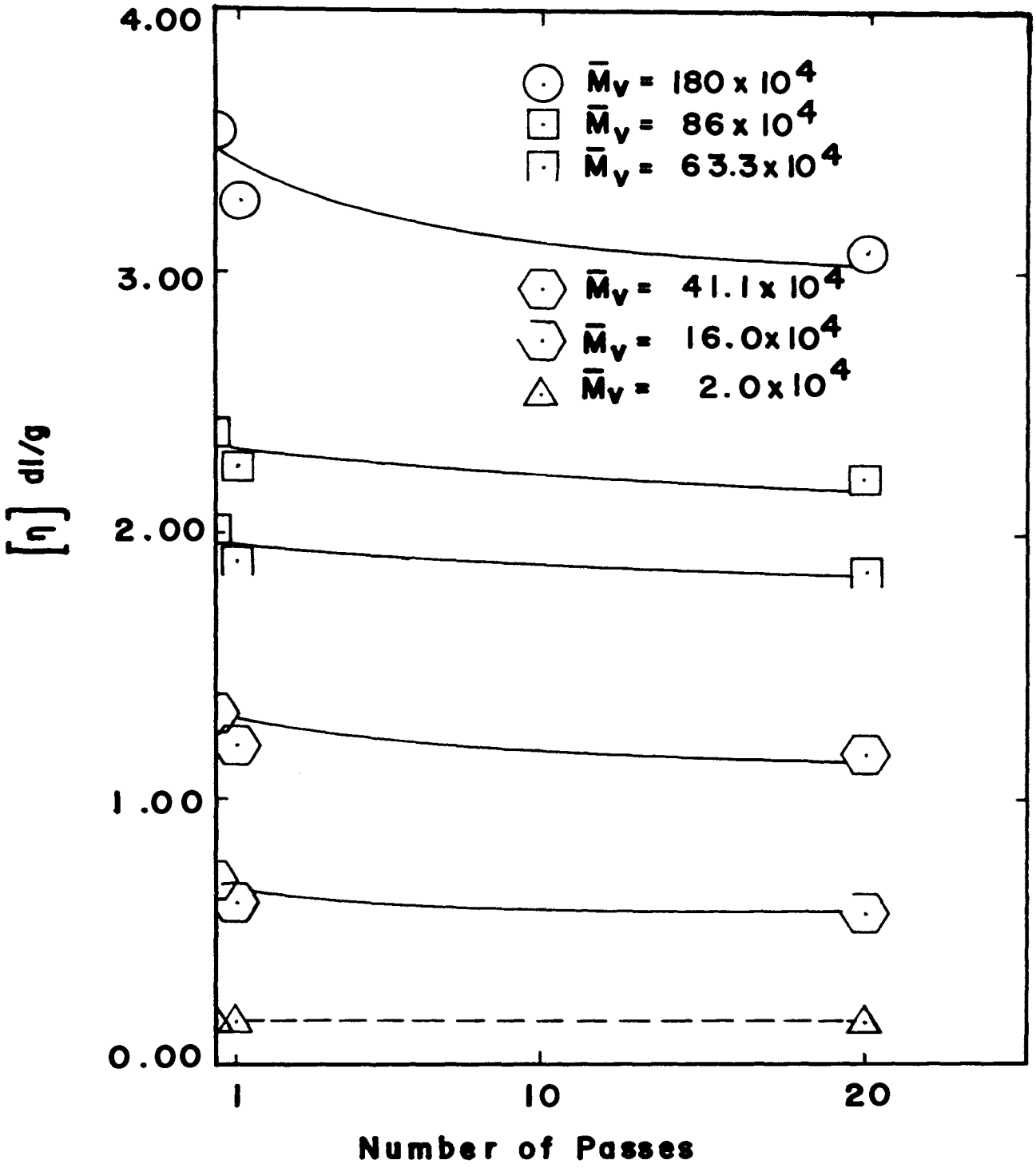

Figure 2. Intrinsic viscosity of polystyrene sample after flowing through the 0.01 in. ID glass capillary tube at 1.4 x 10^5 sec^{-1}.

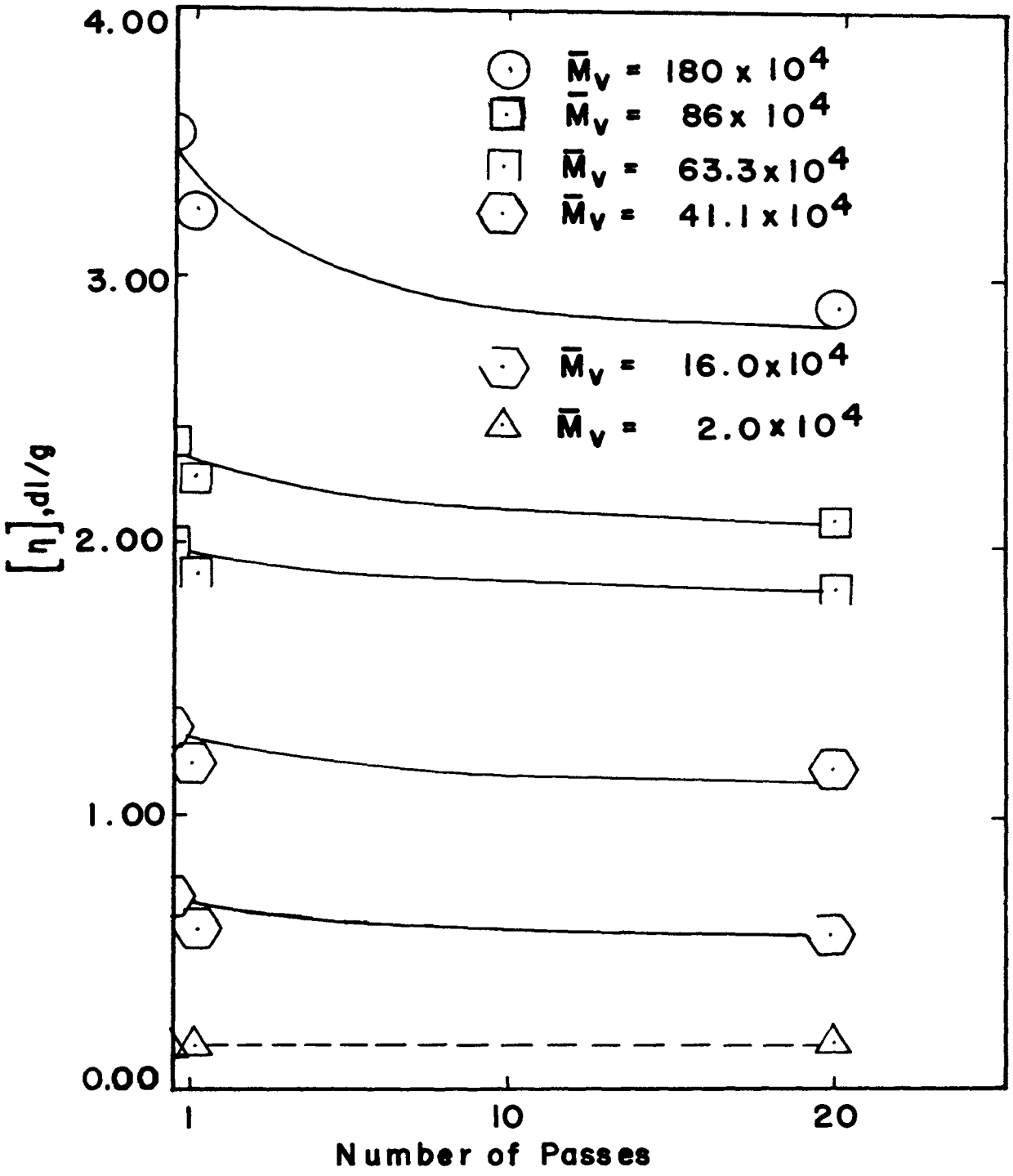

Figure 3. Intrinsic viscosity of polystyrene sample after flowing through the 0.0067 in. ID glass capillary tube at 3.13 x 10^5 sec^{-1}.

of degradation $[\eta]_o - [\eta]$. This agrees directionally with Frenkel's theory[26] that the hydrodynamic shear rate necessary to cause a rupture of a long-chain molecule is inversely proportional to the square of the number of segments in it. Thus, at the same shear rate, relatively high molecular weight polymer should be degraded more easily.

Degradation obtained at 1.40×10^5 sec^{-1} and 3.13×10^5 sec^{-1} through the 0.0100 in. ID and 0.0067 in. ID glass capillary tubes are recorded in Tables V and VI, and Figures 2 and 3, respectively. Figures 2 and 3 show the curves of intrinsic viscosities as a function of pass numbers. For higher molecular weight polymers PS-1, PS-2, PS-3, and PS-4, the intrinsic viscosity drops relatively fast during the first few passes and then levels off. It is apparent that each succeeding pass had less and less influence on the decrease in $[\eta]$ and is an indication that as the size of the polymer is decreased, it is less likely to be degraded.

The results for the extent of degradation as a function of L/D are suprising. Tables VII, VIII, IX, X and XI show the intrinsic viscosities of sample PS-2($[\eta]_o$ = 2.09 dl/g) under various shearing conditions after one pass and after 20 passes for different L/D ratios. The maximum error introduced in any of the $[\eta]$ determinations was $\pm$0.025 dl/g (Appendix G).

TABLE X

DEGRADATION OF POLYMER SAMPLE PS-2

UNDER VARIOUS SHEARING CONDITIONS FOR 1 PASS

Shear Rate Sec.$^{-1}$	dl/g	Diameter in.	Reynold's Number	Length in.	L/D
1.40×10^5	1.96	0.0100	1800	4.4375	443.75
"	1.97	"	"	1.00	100.00
"	1.96	"	"	0.25	25.00
3.13×10^5	1.93	0.0067	"	5.375	800.00
"	1.94	"	"	0.67	100.00
"	1.96	"	"	0.25	31.50
2.22×10^5	1.98	0.0080 (orifice)	"	0.014	1.75

TABLE XI

DEGRADATION OF POLYMER SAMPLE PS-2

UNDER VARIOUS SHEARING CONDITIONS FOR 20 PASSES

Shear Rate Sec.$^{-1}$	dl/g	Diameter in.	Reynold's Number	Length in.	L/D
1.40×10^5	1.91	0.0100	1800	4.4375	443.75
"	1.90	"	"	1.00	100.00
"	1.91	"	"	0.25	25.00
3.13×10^5	1.86	0.0067	"	5.375	800.00
"	1.86	"	"	0.67	100.00
"	1.91	"	"	0.25	37.50
2.22×10^5	1.92	0.0080 (orifice)	"	0.0140	1.75

Figure 4. Variation of k' with molecular weight of polystyrene in toluene at 30°C.

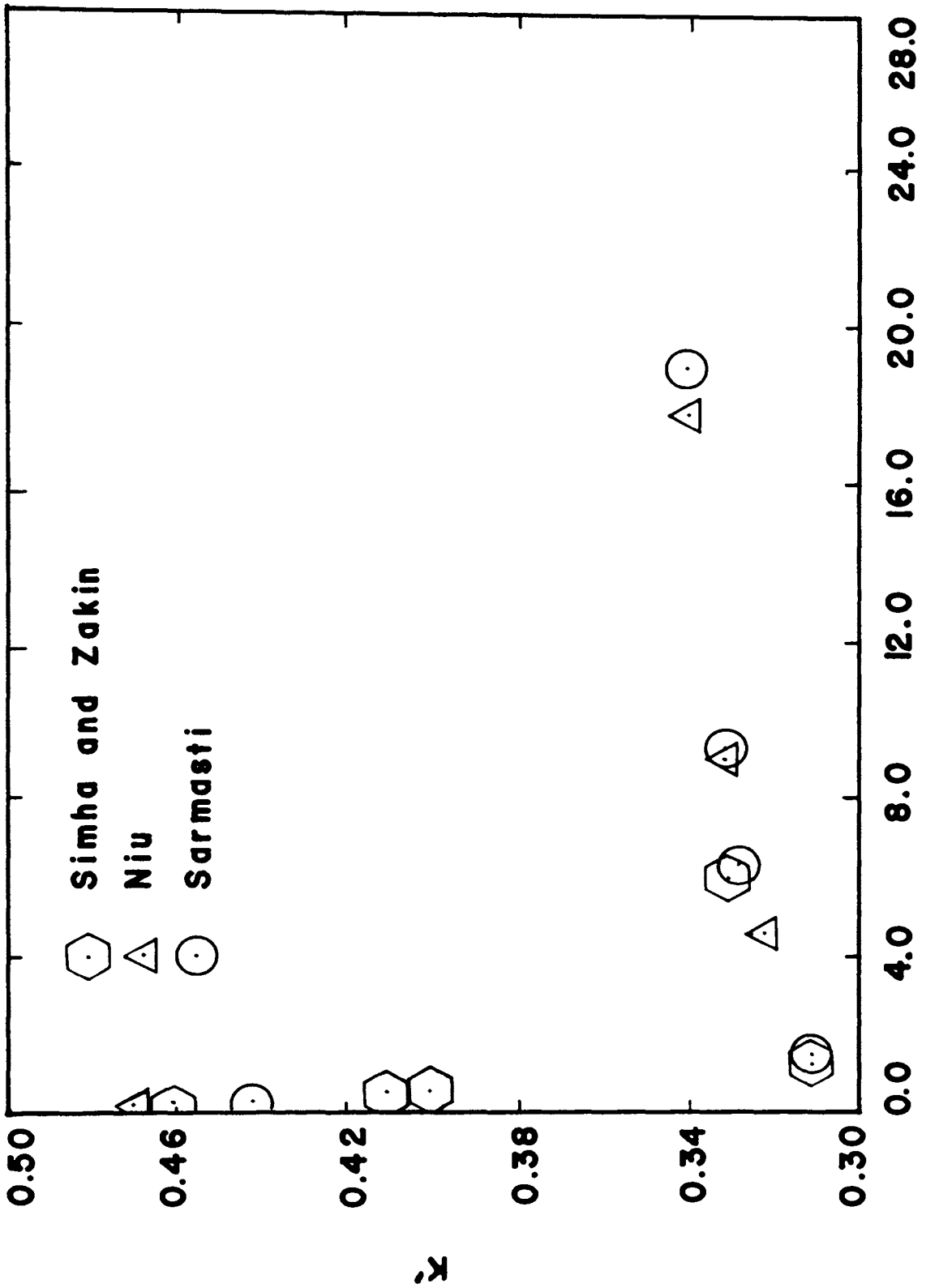
Simha and Zakin
Niu
Sarmasti
0.50
0.46
0.42
0.38
0.34
0.30
κ'
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
$M_v \times 10^{-5}$

Figure 4

The polystyrene samples used in this study must be considered as narrow molecular weight distribution materials on the basis of light scattering, osmotic pressure and ultracentrifuge measurements. The measurements were carefully made and inherent errors do not exceed $\pm 5\%$ for any of the values obtained. On this basis, a calculated M_w/M_n of 1.05 would not be expected to exceed 1.15 at maximum/minimum values for M_w/M_n. Even though the polydispersity for these samples was low, equilibrium molecular weight after many passes was not constant, but seemed to be effected by the initial molecular weight. It can be postulated that under a given set of experimental conditions (shear rate, concentration, solvent, temperature, etc.) that a critical molecular weight exists below which shear degradation does not occur. Figure 5 indicates that perhaps degradation of polystyrene does not occur below $M_v \simeq 150{,}000$ ($[\eta] \simeq 0.5$). This interpretation would be misleading. In reality, one could state that samples having an M_v $<150{,}000$ do not contain a sufficient number of high molecular weight molecules capable of mechanically degrading under the conditions of these experiments. Further, the general correlation of increased degradation with increasing molecular weight could be explained on the basis that it is probable that there are more chains above a critical molecular weight in higher molecular weight polymers than those of lower molecular weights.

Figure 5. $[\eta_o] - [\eta]$ versus log $[\eta_o]$.

(Circles and hexagons represent capillary tubes [D = 0.010 in. and L/D = 444]; triangles and squares represent capillary tube [D = 0.0067 in. and L/D = 800]).

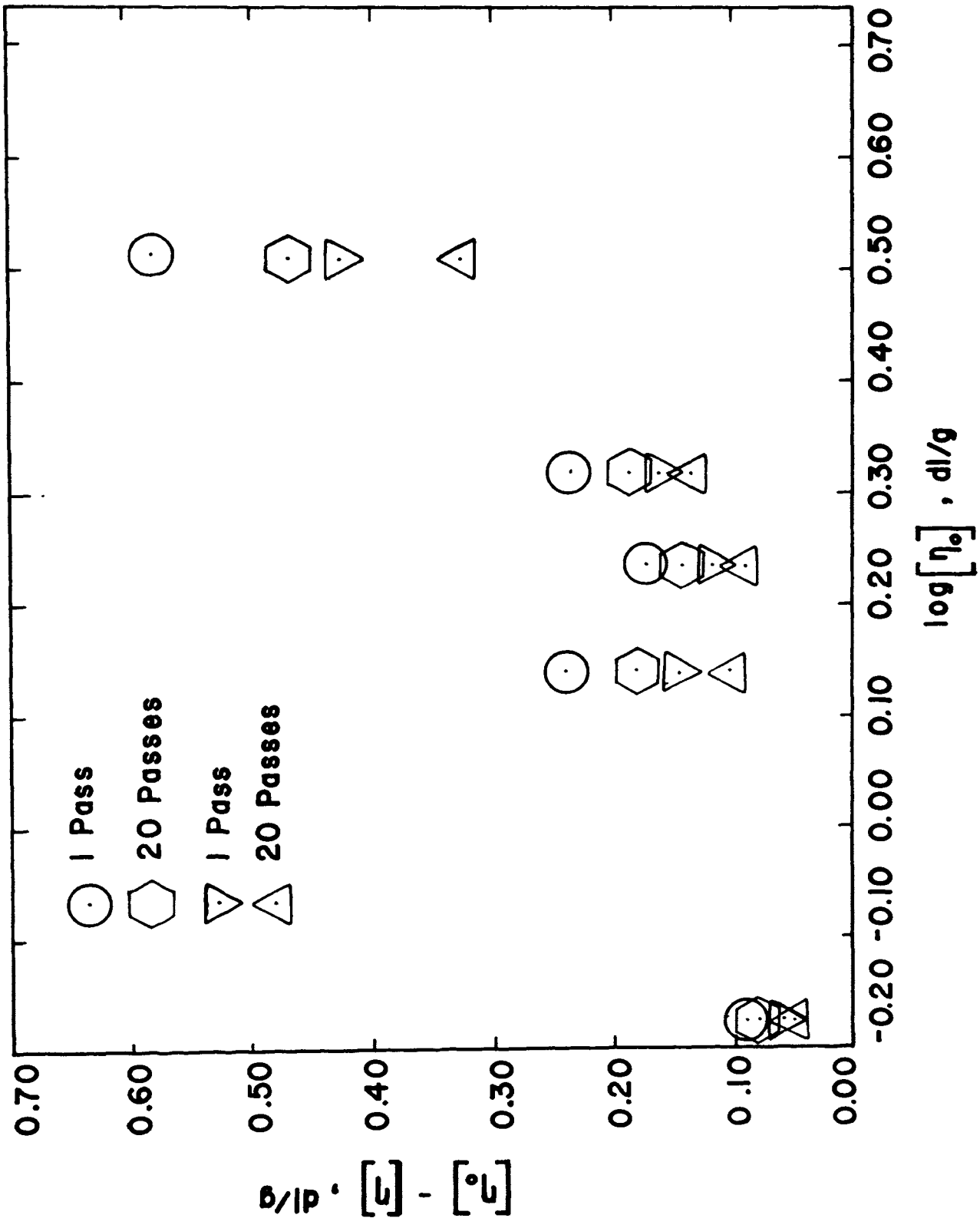
1 Pass
20 Passes
1 Pass
20 Passes
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
-0.20 -0.10 0.00 0.10 0.20 0.30 0.40 0.50 0.60 0.70
log[η], dl/g
[η] - [η]°, dl/g

Figure 5

V. CONCLUSIONS

1. Dilute solution of polystyrene in toluene at 25°C degrades as the result of flow through capillary tubes under conditions of laminar flow and calculated average wall shear rates of $\sim 10^5 - 10^6$ sec^{-1}. For 0.1 weight per cent solutions of narrow molecular weight polystyrene samples having molecular weight ranging from 1.80×10^6 to 2.0×10^4, it was found that the lower initial molecular weight of the polymer, the lower the extent of degradation.

2. For higher molecular weight polystyrene samples $[\eta]$ drops relatively fast during the first several passes and then levels off. Succeeding passes had less influence on the decrease in $[\eta]$ and is an indication that as the size of the polymer is decreased, it is less likely to be degraded.

3. The experimental results indicate that for a given M_v, the extent of degradation is a function of the molecular weight distribution as well as the initial molecular weight. The molecular weight distribution, M_w/M_n, may be specific for a given method of polymerization or fractionation.

4. The extent of degradation at shear rates of $\sim 10^5 - 10^6$ sec^{-1} appears to be independent of the L/D ratio.

5. For high molecular weight polystyrene (750,000) in toluene, k', the Huggins constant, is about 0.34 and for low molecular weight polystyrene samples this constant has a value of 0.44

VI . APPENDICES

The physical properties of toluene are given in Appendix A. Appendix B contains a scanning electron micrograph of the brass orifice. The operational procedure for the degradation test system is given in Appendix C. All calculations for calibration are shown in Appendix D. All experimental data for the intrinsic viscosity measurements collected during the investigation are listed in Appendix E. All sample calculations and a typical plot of $\eta sp/c$ versus c and $(\ln \eta_r)/C$ versus C are given in Appendix F. Appendix G is an error analysis for the intrinsic viscosity measurement. Appendix H is the nomenclature.

APPENDIX A

Physical Properties of Toluene

Sample	Temperature °C	Density		Absolute Viscosity	
		Measured	Literature	Measured	Literature*
		g/ml		Centipoise	
Toluene (A)	30	0.8556	0.8577	0.5177	0.5187
Toluene (B)	30	0.8573	0.8577	0.5200	0.5187

*Ref. (23, 24)

APPENDIX B

Micrograph of Brass Orifice

APPENDIX C

Operational Procedure for the Degradation Test System

1. Charge the process fluid into the glass cylinder. Leave valve (2) open throughout the test.
2. Open valve (1), (3) and (4), close valve (5) and stopcock (7), turn the three-way stopcock to the inlet of nitrogen gas. Then open valve (6), and the low-pressure nitrogen gas is introduced to force the fluid in the glass cylinder to flow into the reservoir.
3. When no fluid is remaining in the glass cylinder, close valve (4). By operating valve (3), (5) and the regulator on the nitrogen gas cylinder, the nitrogen gas from the cylinder is regulated to the desired driving pressure. Then leave valves (3) and (5) closed.
4. Close valve (1), turn the three-way stopcock to the glass-discharge line and open stopcock (7). Then open valve (4) and (5), and the fluid in the reservoir is forced to flow through the capillary tube and discharge into the glass cylinder.
5. When no more fluid jets from the capillary, close valve (5), then open valve (3) and discharge the high-pressure nitrogen gas to the air.
6. Repeat steps 2 to 5, make another pass.

APPENDIX D

Calibration of Tubes

The most important variable in capillary viscometry is diameter. Thus, an accurate calibration of the capillary tube used is important for obtaining reliable measurements. The usual procedure followed in calibrating the capillary tube is to use a fluid of known viscosity and density, and applying the Hagen-Poiseuille law for laminar flow of Newtonian fluid, Nikuradse law for turbulent fluid, and the equation for flow through an orifice to the experimental data:

$$D = 2(8QL\ \mu/\pi\ \ \Delta P)^{1/4} \qquad (1)$$

where μ is the viscosity, Q is the flow rate, L is the capillary length and ΔP is the pressure drop across the tube (due to the high L/D ratio, the end effect is negligible).

A. Capillary Tube Diameters

1. Newtonian fluid

$$D = 2(8QL\ \mu/\pi\ \Delta P)^{1/4} \qquad (1)$$

$W = 0.3607$ g/sec

$L = 4.4375$ in.

$$\rho = (0.8623 \text{ g/ml})(62.43) = 53.83 \frac{\text{lbm}}{\text{cu ft}}$$

(at 25°C)

$$\mu = 0.5516 \text{ centipoise} = 0.5516 \times 6.72 \times 10^{4} \frac{\text{lbm}}{\text{ft.sec.}}$$

$$g_c = 32.20 \frac{\text{lbm}}{\text{lbf}} \cdot \frac{\text{ft}}{(\text{sec})^2}$$

$$\Delta P = 100 \text{ Psi} = 100 \times 144 \text{ lbf/sq.ft.}$$

$$D = \frac{128\mu}{\rho g_c \pi} \left[\frac{LW}{(\Delta P)}\right]^{1/4}$$

$$D = \frac{(\text{lbm/ft sec})(\text{ft})(\text{lbm/sec})}{(\text{lbm/cu ft})(\text{lbm/lbf})(\text{ft/sq sec})(\text{lbf/sq ft})}$$

$$D = \frac{(128)(0.5516 \times 6.72 \times 10^{-4})}{(53.83)(32.2)(\ )} \cdot \left[\frac{(4.4375/12)(0.21/453.59)}{(30 \times 144)}\right]^{1/4}$$

$$D = 0.00084 \text{ ft}$$

$$D = 0.0101 \text{ in.}$$

2. Turbulent

$$\frac{1}{\sqrt{f}} = 4.0 \log (N_{r_c} \sqrt{f}) - 0.40 \qquad (2)$$

$$f = \frac{(P/\rho)(D/L)}{(V^2/2g_c)}$$

$w = \rho VS$

$N_{R_c} = \frac{\rho VD}{\mu}$

f = friction factor, dimensionless

s = duct cross-sectional area, ft^2

N_{R_c} = Reynold's number, dimesionless

V = velocity, ft/sec

I. Velocity

$$V = \frac{4Q}{\pi D^2} = \frac{4W}{\rho \pi D^2} = \frac{(cc/sec)(ft^3/cc)}{(ft^2)}$$

$$= \frac{(0.33/453.59)(4)}{(\pi)\ (53.83)\ (0.0104/12)^2}$$

$$V = 25.10 \text{ ft/sec}$$

II. Reynold's Number

$$N_{R_c} = \frac{DV\rho}{\mu} \quad \frac{(ft)(ft/sec)(\frac{lbm}{cu\ ft})}{(lbm/ft\ sec)}$$

$$= \frac{(0.0104/12)(25.1)(53.83)}{(0.5516 \times 6.72 \times 10^{-4})} = 3075$$

3. Orifice Method

$$D = \left(\frac{8W^2}{\pi^2 g_c \rho \Delta P}\right)^{1/4} \qquad (3)$$

$$D = \left[\frac{(lbm/sec)^2}{(\frac{lbm}{lbf} \cdot ft/sq\ sec)(lbm/cu\ ft)(lbf/sq\ ft)}\right]$$

$$= \frac{(8)(0.1528/453.59)^2}{(32.2)(53.83)(2 \times 144)}^{1/4}$$

$D = 0.00066$ ft.

$D = 0.0080$ in.

APPENDIX E

Tables

TABLE XII

INTRINSIC VISCOSITY MEASUREMENT DATA

No.	Conc. g/dl	Efflux Time sec.	Relative Viscosity	Specific Viscosity	Reduced Viscosity dl/g	Inherent Viscosity dl/g
Sample PS-1, toluene efflux time = 160.9 sec						
1	0.24	331.10	2.0578	1.0578	4.407	3.007
2	0.18	280.80	1.7555	0.7555	4.197	3.135
3	0.0667	240.55	1.2505	0.2505	3.757	3.353
4	0.050	197.70	1.1833	0.1833	3.666	3.3667
5	0.025	175.35	1.0878	0.0878	3.592	3.362
Sample PS-2, toluene efflux time = 160.9 sec						
1	0.36	311.30	1.9347	0.9347	2.596	1.833
2	0.24	254.10	1.5793	0.5793	2.414	1.905
3	0.18	228.65	1.4212	0.4212	2.341	1.952
4	0.09	193.70	1.2000	0.2000	2.225	2.02
Sample PS-3, toluene efflux time = 160.8 sec						
1	0.40	298.60	1.8558	0.8558	2.140	1.546
2	0.30	260.10	1.6165	0.6165	2.057	1.578
3	0.20	222.80	1.3847	0.3847	0.926	1.628
4	0.10	190.30	1.1827	0.1827	1.827	1.679

TABLE XII (CONTINUED)

No.	Conc. g/dl	Efflux Time sec.	Relative Viscosity	Specific Viscosity	Reduced Viscosity dl/g	Inherent Viscosity dl/g
Sample PS-4, toluene efflux time = 160.9 sec						
1	0.540	300.0	1.8645	0.8645	1.600	1.154
2	0.360	247.00	1.5350	0.5350	1.486	1.191
3	0.270	122.85	1.3850	0.3850	1.426	1.207
4	0.135	190.45	1.1836	0.1836	1.360	1.249
5	0.067	175.40	1.0901	0.0901	1.335	1.280
Sample PS-5, toluene efflux time = 160.7 sec						
1	1.20	324.30	2.0160	1.0160	0.847	0.584
2	0.90	278.20	1.7290	0.7290	0.810	0.610
3	0.60	234.65	1.4574	0.4574	0.764	0.644
4	0.30	195.60	1.2157	0.2157	0.719	0.650
Sample PS-6, toluene efflux time = 160.9 sec						
1	5.00	327.10	2.0329	1.0329	0.206	0.142
2	3.75	263.75	1.7030	0.7030	0.187	0.142
3	2.50	232.35	1.4440	0.4440	0.177	0.143
4	1.25	193.70	1.2038	0.2039	0.163	0.143
5	0.62	176.40	1.0963	0.0963	0.154	0.143

TABLE XIII

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.010 IN., L = 4.4375 IN.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.3300	1.790	0.790	2.3900	1.760
2	0.2200	1.490	0.490	2.2300	1.835
3	0.1650	1.360	0.360	2.1800	1.845
4	0.0825	1.175	0.175	2.1200	1.920
5	0.0412	1.083	0.083	2.0100	1.935
c. 20 passes					
1	0.60	2.566	1.566	2.6100	1.5700
2	0.40	1.956	0.956	2.3900	1.6800
3	0.30	1.675	0.675	2.2500	1.7200
4	0.15	1.313	0.315	2.0900	1.8200

TABLE XIV

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.0067 in., L = 5.375 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.440	2.08	1.08	2.45	1.660
2	0.294	1.68	0.68	2.28	1.740
3	0.220	1.48	0.48	2.18	1.795
4	0.110	1.25	0.23	2.09	1.870
5	0.055	1.11	0.11	2.00	1.905
c. 20 passes					
1	0.540	2.3340	1.3340	2.47	1.57
2	0.360	1.8210	0.8210	2.28	1.66
3	0.270	1.5886	0.5886	2.18	1.71
4	0.135	1.2710	0.2710	2.01	1.77

TABLE XV

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.010 in., L = 1.00 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.396	1.9740	0.9740	2.46	1.72
2	0.264	1.6040	0.6040	2.29	1.78
3	0.198	1.4350	0.4350	2.20	1.82
4	0.099	1.2060	0.2060	2.08	1.89
c. 20 passes					
1	0.420	1.9996	0.9996	2.38	1.650
2	0.280	1.6244	0.6244	2.23	1.733
3	0.210	1.4150	0.4515	2.15	1.774
4	0.105	1.2130	0.2130	2.03	1.850

TABLE XVI

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.0067 in., L = 0.67 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.48	2.2096	1.2096	2.52	1.65
2	0.32	1.7456	1.7456	2.33	1.74
3	0.24	1.5376	0.5376	2.24	1.79
4	0.12	1.2544	0.2544	2.12	1.89
c. 20 passes					
1	0.4500	2.0665	1.0665	2.370	1.600
2	0.3000	1.6510	0.6510	2.170	1.670
3	0.2250	1.4770	0.4770	2.120	1.730
4	0.1125	1.2220	0.2220	1.985	1.785

TABLE XVII

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.0067 in., L = 0.25 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.48	2.23	1.23	2.560	1.67
2	0.36	1.8470	0.8470	2.350	1.71
3	0.18	1.3970	0.397	2.200	1.85
4	0.09	1.1860	0.186	2.070	1.90
c. 20 passes					
1	0.48	2.2050	1.2050	2.510	1.645
2	0.36	1.8565	0.8565	2.380	1.720
3	0.18	1.3850	0.3850	2.140	1.810

TABLE XVIII

INTRINSIC VISCOSITY MEASUREMENT DATA

GLASS CAPILLARY TUBE (D = 0.010 in., L = 0.25 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.2000	0.2000	2.2255	2.0235
b. 1 pass					
1	0.48	2.231	1.231	2.560	1.670
2	0.36	1.848	0.848	2.350	1.710
3	0.18	1.398	0.398	2.200	
4	0.09	1.186	0.186	2.070	1.900
c. 20 passes					
1	0.470	2.1678	1.1678	2.490	1.650
2	0.350	1.8270	0.8270	2.360	1.720
3	0.175	1.3760	0.3760	2.150	1.8150

TABLE XIX

INTRINSIC VISCOSITY MEASUREMENT DATA

BRASS ORIFICE (D = 0.0080 in., L = 0.014 in.)

No.	Conc. g/dl	Relative Viscosity	Specific Viscosity	Reduced Viscosity	Inherent Viscosity
PS-2 in toluene at 30°C					
a. Zero passes					
1	0.36	1.9347	0.9347	2.5964	1.8333
2	0.24	1.5793	0.5793	2.4137	1.9050
3	0.18	1.4212	0.4212	2.3408	1.9522
4	0.09	1.200	0.2000	2.2255	2.0235
b. 1 pass					
1	0.400	2.0320	1.0320	2.5800	1.7700
2	0.265	1.6280	0.6280	2.3700	1.8350
3	0.200	1.4550	0.4550	2.2750	1.8750
c. 20 passes					
1	0.400	2.0345	1.0345	2.5800	1.7700
2	0.265	1.6240	0.6240	2.3700	1.8350
3	0.200	1.4545	0.4545	2.2750	1.8750

APPENDIX F

Intrinsic Viscosity and Huggins Constant

A typical plot of η_{sp}/C versus C and $(\ln \eta_r)/C$ is shown in Figure 6, which is the result of the degradation test polystyrene , PS-2, solution in 0.0100 in. ID glass capillary tube under 18 Psi for 20 passes, the viscosity measurement data are given in Appendix E.

According to Eq. (6) and Eq. (7), the intercept of the straight lines is the intrinsic viscosity of the polymer:

$$\frac{\eta_{sp}}{c} = [\eta]_1 + k' [\eta]_1^2 C \qquad (6)$$

$$\frac{\ln \eta_r}{c} = [\eta]_2 - k'' [\eta]_2^2 C \qquad (7)$$

$$[\eta]_1 = [\eta]_2 = [\eta] = 1.90$$

The slope of η_{sp}/C is 1.1990, thus

$$k'[\eta]^2 = 3.90$$

$$k' = \frac{k'[\eta]^2}{[\eta]^2} = 0.327$$

$$k'' = \frac{k''[\eta]^2}{[\eta]^2} = 0.1700$$

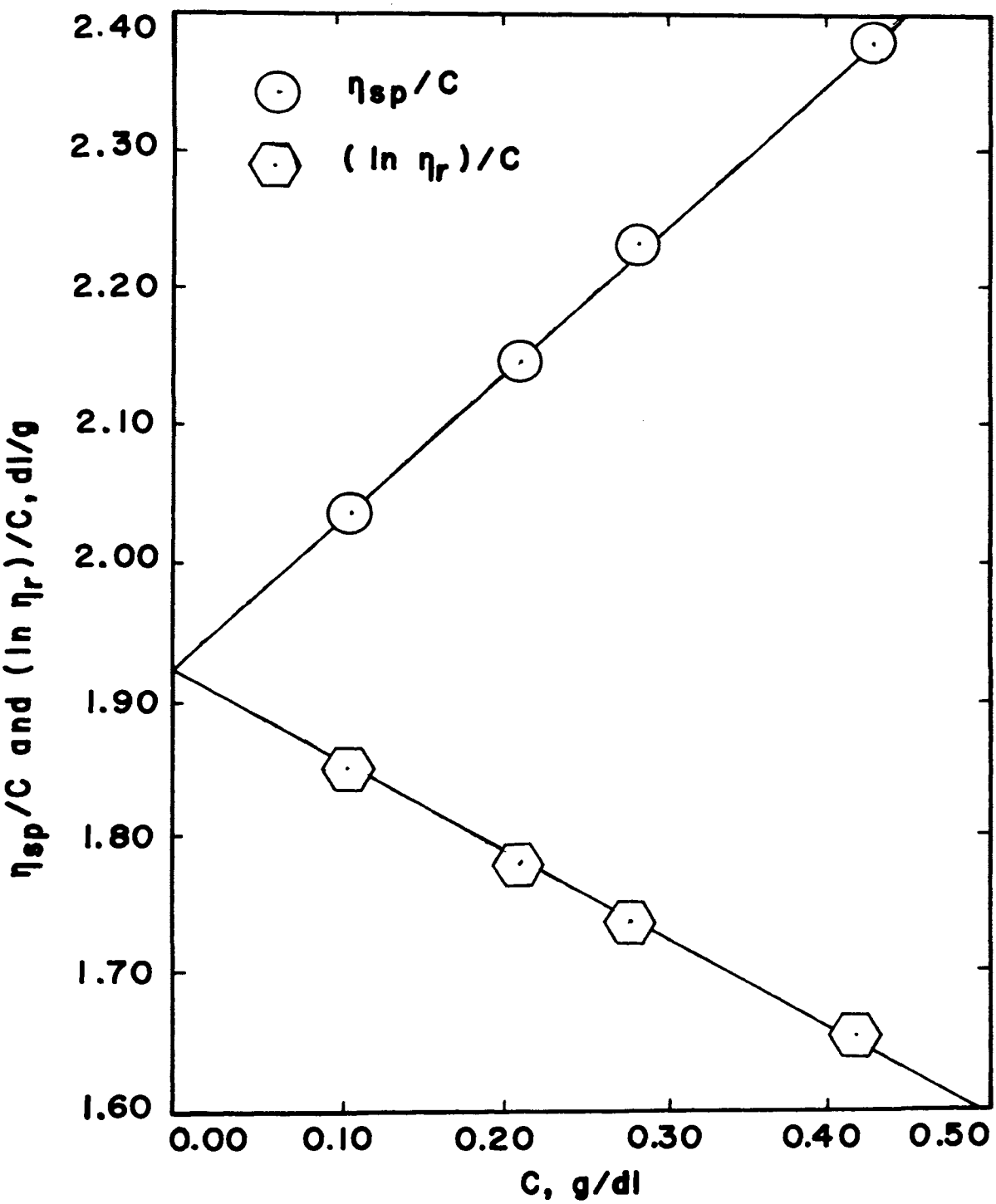

Figure 6. Reduced and inherent viscosity concentration curves for the degradation of polymer sample PS-2 (M_v = 86 x 10^4) in 0.0100 in. ID and L/D = 100 glass capillary tube at 1.40 x 10^5 sec^{-1}.

APPENDIX G

Error Analysis for Intrinsic Viscosity Measurement

In the preparation of solution for viscosity measurement, the error in the volume reading on the volumetric flask was ± 0.10 ml.; the error in the weight reading of the balance was ± 0.0002 by dissolving 0.1 g polymer into 100 ml of solution, the error of the concentration can be calculated as:

$$C = \frac{w}{v} \quad \text{and} \quad c + \Delta C = \frac{w + \Delta w}{v + \Delta v}$$

where $w = 0.109$; $\Delta w = 0.0002$g, $V = 100$ ml and $\Delta V = 0.10$ ml, then,

$$\Delta C = \frac{w + \Delta w}{V + \Delta V} - \frac{w}{V} = \frac{V\,\Delta w - w\,\Delta v}{V(V + \Delta V)}$$

$$= \frac{100 \times 0.0002 - 0.10 \times 0.1}{10000 + 10} = \frac{0.3}{10010}$$

$$= 3 \times 10^{-5} \text{ g/ml or } 3 \times 10^{-3} \text{ g/dl}$$

Thus, the concentration is 0.100 - 0.003 g/dl.

The temperature of the water bath can be maintained within $30.00 \pm 0.01°C$. The error introduced by any small temperature difference is negligible. The efflux time was measured with an accurate electric timer which can be read within ± 0.1 second. The error of the relative viscosity

can be shown by

$$\eta_r = t/to$$

where t and to are the efflux time of solution and solvent, respectively, and

$$\eta_r + \Delta\eta_r = \frac{t + \Delta t}{t_o + \Delta t}$$

then

$$\Delta\eta_r = \frac{(t-t_o)\Delta t}{t_o(T_o + \Delta t)}$$

the highest value of t in our experiments is 327.50 sec., the lowest value of t_o is 160.8 sec, thus we obtain the maximum error in η_r as

$$\Delta\eta_r = \frac{(327.50 - 160.8)0.1}{160.8(160.8 + 0.1)} = 0.0006$$

and $\Delta\eta_{sp} = \Delta\eta_r$.

The maximum error introduced in the reduced viscosity can be calculated from the information given above,

$$\frac{\eta_{sp}}{C} + \left(\frac{\eta_{sp}}{C}\right) = \frac{\eta_{sp} + \Delta\eta\ sp}{C + \Delta C}$$

$$\left(\frac{\eta_{sp}}{C}\right) = \left(\frac{\eta_{sp} + \Delta\eta_{sp}}{C + \Delta C}\right) - \frac{\eta_{sp}}{C} = \frac{C\,\Delta\eta_{sp} - \eta_{sp}\,\Delta C}{C(C + \Delta C)}$$

The minimum value for η_{sp} in this study is 0.0109.

$$\Delta\left(\frac{\eta_{sp}}{C}\right) = \frac{0.10 \times 0.0006 - 0.0109 \times 0.003}{0.01 + 0.0003} = 0.025 \text{ dl/g}$$

Thus, the uncertainty in the evaluation of the intrinsic viscosity is $\pm$0.025 dl/g which is about 0.6% of the highest intrinsic viscosity value ($[\eta] = 3.52$) that we obtain.

APPENDIX H

Nomenclature

a	=	exponent in equation (5)
c	=	concentration
Δc	=	absolute value of error in concentration measurement
d	=	diameter, inches
f	=	friction factor, dimensionless
ID	=	inside diameter, inches
OD	=	outside diameter
k'	=	Huggins constant
k''	=	constant in equation (7)
k	=	constant in equation (5)
L	=	capillary length, inches
$\bar{M}_n$	=	number average molecular weight, grams/gram-mole
$\bar{M}_v$	=	viscosity average molecular weight, grams/gram-mole
$\bar{M}_w$	=	weight average molecular weight, grams/gram-mole
ΔP	=	pressure drop across the tube, lbf/ft^2
Q	=	flow rate, cc/sec
R	=	radius of tube, inches
t	=	efflux time of solution, seconds
t_o	=	efflux time of solvent, seconds
Δt	=	absolute value of the error in time reading
V	=	bulk velocity, ft/sec
v	=	velocity of flow along the tube, ft/sec
W	=	flow rate, g/sec
w	=	weight, grams

Δw = absolute value of the uncertainty in the weight reading of the balance

π = geometric constant (=3.1416)

ρ = density, grams/milliliter

μ = absolute viscosity, pound/ft. sec.

N_{R_c} = Reynold's number

η_r = relative viscosity

η_{sp} = specific viscosity

$[\eta]_1$ = intrinsic viscosity calculated from plots of η_{sp}/c versus c, deciliters/gram

$[\eta]_2$ = intrinsic viscosity calculated from plots of $(\ln\eta_r)/c$ versus c, deciliters/gram

$[\eta]$ = true intrinsic viscosity, deciliters/gram

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